

Molecular Mechanics Studies (MM4) of Sulfides and Mercaptans

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ABSTRACT: The MM4 force field has been extended to the title class of compounds. The vibrational spectra, structures, conformational equilibria, and heats of formation have been studied for 47 conformers of 29 compounds. In general, the properties may be calculated with accuracy that is competitive with that for hydrocarbons. The structures are better fit than previously because of the inclusion of a torsion–bend interaction term, which has its origin in the lone pair (Bohlmann) effect. Available experimental data do not suffice to yield detailed torsional potentials, or geometries as a function of torsion angle, and these quantities were determined by *ab initio* calculations at the MP2/6-31G* level. The rms error in the calculated frequencies of seven representative structures (with a total of 64 experimental and 96 *ab initio* frequencies) is 25 cm⁻¹. The heats of formation for 23 compounds have a weighted rms error of 0.36 kcal/mol. © 1997 John Wiley & Sons, Inc. *J Comput Chem* 18: 1827–1847, 1997

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Introduction

Early force fields did a creditable job calculating many properties for a wide series of molecules.¹ The structures and properties were

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always experimentally based. More recently, it has been possible to carry out *ab initio* calculations from which many structures and properties can be obtained with an accuracy that is competitive with experiment. Since experiments sometimes contain ambiguities, or misinterpretations, this gives us two independent methods for determining structures, and most other properties, of molecules. When the two agree, we can be reasonable confident of the data. When they disagree, additional studies are necessary. As force field calculations developed in accuracy over the years, and as *ab initio* calculations became available, it became clearer just where the major errors in the calculations were to be found. The early force fields

(which Hagler² has called Class 1) were harmonic and diagonal (with respect to the explicit terms put into the force constant matrix). It became evident that, while such a force field was adequate for many purposes, a more general force field had to be anharmonic, and it had to contain some explicit off-diagonal elements, and Hagler referred to such a force field as Class 2. A good Class 2 force field may be considered as a physicist's force field. It is purely mechanical, concerned with stretchings, bendings, force constants, and the like. We have suggested³ that a Class 3 force field is a chemist's force field. To what is described above for a Class 2 force field, we must also add those many quantities which are chemically explicit, and depend not only on such things as masses and force constants, but also depend on what particular atom is present, and the characteristic properties of that particular atom, of which the presence or absence of lone pairs or acidic hydrogens is especially important. Of course, real force fields are not usually exactly Class 1, 2, or 3, but MM2 was close to Class 1, while MM3⁴ is close to Class 2.

Earlier studies on the MM4 force field have outlined for saturated hydrocarbons just how this force field is constructed, and, for compounds of this class, there is no difference between Class 2 and Class 3.⁵ So, we may consider the MM4 force field as Class 3 for saturated hydrocarbons. Unsaturated hydrocarbons, however, require a Class 3 force field to account for some properties, in particular, hyperconjugation.⁶ The next step is to add heteroatoms to MM4, to allow for the chemical nature of properties as determined by the force field, and thus develop a full Class 3 force field. We have chosen sulfur, which would appear to be a relatively simple and straightforward example, with which to begin.⁷

Chemical effects, which have so far been demonstrated to be important in developing force fields, include hyperconjugation,⁶ electronegativity,⁸ and the Bohlmann⁹ and anomeric effects.¹⁰ These have been explicitly taken into account to some level of approximation in many previous force fields, including MM3.

Structure and Energies of Sulfides and Mercaptans

We earlier presented the MM3 treatment of compounds of the present class, alkyl sulfides.¹¹

There were some small errors in how well MM3 could deal with these compounds, and one very significant systematic error in geometries. This error can be illustrated with reference to methylethylsulfide. We found in this case with MM3 that we could not calculate the moments of inertia correctly for both the anti and for the gauche conformations at the same time with the parameter set in MM3. The fundamental problem was that the C—C—S angle experimentally opened up by several degrees as the molecule went from the anti to the gauche conformation, while the amount of opening with MM3 was only about 1.5°, mainly as a result of van der Waals interactions. Hence, we could compromise these values and fit the experimental data somewhat inaccurately. More recently it has been possible to do reasonably good *ab initio* calculations (optimized at the MP2/6-31G* level) on the molecule as a function of torsion angle.^{7, 12} The variation in the C—C—S angle with torsion angle is plotted in Figure 1. Note that the MM3 curve fits the *ab initio* curve after a fashion, but certainly not very well. The MM3 value for the C—C—S angle is more than 2° too large at 180°, more than 2° too small at 90°, and about 1° too small at 0°. This variation cannot be mimicked with MM3 by any reasonable parameter change. Rather, it results from something that is left out of the basic MM3 force field. This proves to be a torsion-bend interaction. When this quantity is added, we can improve the fit of the MM4 calculated variations of bond angle with torsion angle as shown in Figure 1. The corresponding fit of the MM4 calculations of the moments of inertia of the *trans*- and *gauche*-methylethylsulfide are then better for MM4 than they were for MM3 in that the errors have been reduced by about a factor of 2. In other examples the errors are reduced even more, as will be discussed later.

Force fields are developed to fit sets of experimental or *ab initio* data, and as long as the data are few, they can always be fit quite well. A meaningful fit to the data, however, is required to be useful. This in turn requires that we understand why the data are as they are. In the above case, why is it that the C—C—S bond angle opens as the molecule undergoes internal rotation? The answer to this question is dependent upon the chemical, as opposed to physical, nature of the force field element required in this case.

We chose sulfur to start with in the MM4 development of heteroatom force fields, thinking that it is chemically more like carbon than other first row atoms would be, and there should be fewer and

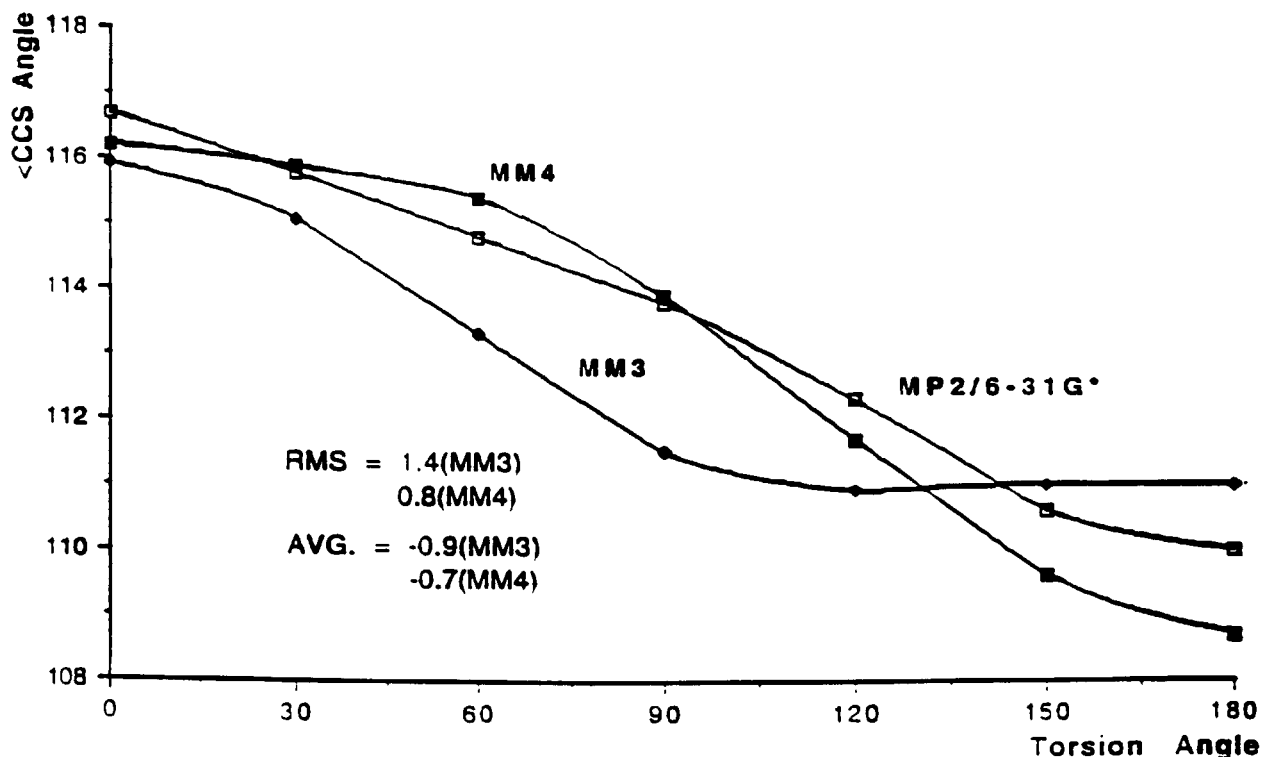


FIGURE 1. The variation of the CCS angle in methylethylsulfide as a function of the CCSC torsional angle.

smaller "chemical effects" to worry about. Thus the first row atoms have lone pairs of electrons, and pronounced chemical effects that result from these lone pairs. For sulfur, while it does have lone pairs, the C—S bond is much longer than the corresponding bonds with first row atoms, and the interaction of the lone pairs with the rest of the system is correspondingly reduced. This interaction is, however, not negligible. If we look at methyl ethyl sulfide as an example, and consider that the sulfur atom contains two lone pairs of electrons, in approximately sp^3 hybrid orbitals, then in the trans conformation the dihedral angle of the methyl group of the ethyl group puts it between those lone pairs. As we rotate that methyl group with respect to the other methyl, from 180° (trans) to 0° (cis), the angles that the methyl makes with respect to the lone pairs change so as to become 120° with respect to each lone pair at the cis limit. Any interaction of this rotating methyl with the lone pairs would be expected to be describable by a Fourier series containing V_1 , V_2 , and V_3 terms (possibly more). Since we are interested in the bending of a bond angle, this would be most conveniently treated as a torsion-bend element to

be added to the force constant matrix, and the energy of the interaction should be formulated in the following way:

$$E_{TB} = 2.51124 * \{ K_{TB1}(\Delta\theta_1 + \Delta\theta_2)(1 + \cos \omega) \\ + K_{TB2}(\Delta\theta_1 + \Delta\theta_2)(1 - \cos 2\omega) \\ + K_{TB3}(\Delta\theta_1 + \Delta\theta_2)(1 + \cos 3\omega) \}$$

If this physical picture for the interaction is correct, then a number of things follow. First, the torsion-bend constants (K_{TBn}) will probably be near zero when the sulfur atom is at the center of the unit under examination (i.e., a C—S—C bond angle), but will have nonzero values when sulfur is at the end (C—C—S).¹³ There is no such term in an alkane, because of the lack of lone pairs. Such a term is expected in ethers, amines, etc., and it has been found.⁷ So now it is simply a matter of picking the correct numerical values for K_{TBn} so as to represent as best we can with MM4 what the *ab initio* calculation/experiment tells us.

This was done, and the results for methylethylsulfide are shown graphically in Figure 1. One can pick suitable constants so as to much better fit the *ab initio*/experimental values for the bond angle

and how it changes upon rotation. In Figures 2 and 3 we similarly fit the H—C—S angle in methanethiol, and the H—C—S angle in dimethylsulfide. It is evident that the fits are much better including this term (MM4), than without it (MM3).

Figure 4 shows the corresponding curves for the C—S—C angle in dimethylsulfide. Here there is no term for the torsion-bend type required in principle, according to our earlier rationalizations, and indeed we see that there is none required in practice.

We also studied the ethanethiol H—C—S interaction, which shows this effect, and the ethanethiol C—S—H (Fig. 5) and methylethylsulfide C—S—C angles (Fig. 6), which do not show this effect. The figures are as expected, and they are available as Supplementary Material. Our conclusion is that this torsion-bend term is quite important in the case of sulfides, and a series of 29 bond angles which involve this effect can be reproduced by MM4 with an rms discrepancy relative to the MP2/6-31G* calculations of 0.5° , compared with a corresponding rms discrepancy of 1.8° with MM3. We estimate that the absolute accuracies of the angles in these compounds are about 1° in the *ab*

initio calculations, while the relative accuracies are probably about 0.5° , so MM4 fits the available structural data as well as would be meaningful.

With the addition of this torsion-bend term, essentially the same general force field was used for sulfides as was previously used for MM3 plus the hydrocarbon changes used to go from MM3 to MM4, and all of the parameters were optimized in the usual way. The final parameter set obtained is given in Table I.

A total of 15 compounds were examined in terms of their structures, energies and other related molecular properties including dipole moments.

Their geometries are presented in Tables II–XIII, compared with experimental values or *ab initio* results.^{21–60} The results have been significantly improved over those from MM3 and are consistent with the available ED and MW data. Structural information for some selected compounds is shown in Figures 7, 10, and 11. The moments of inertia in MM4 are calculated as r_z values, which may be directly compared to the corresponding MW data, while they are r_g values in MM3. Normally, when we go from a r_z geometry to a r_g geometry, the

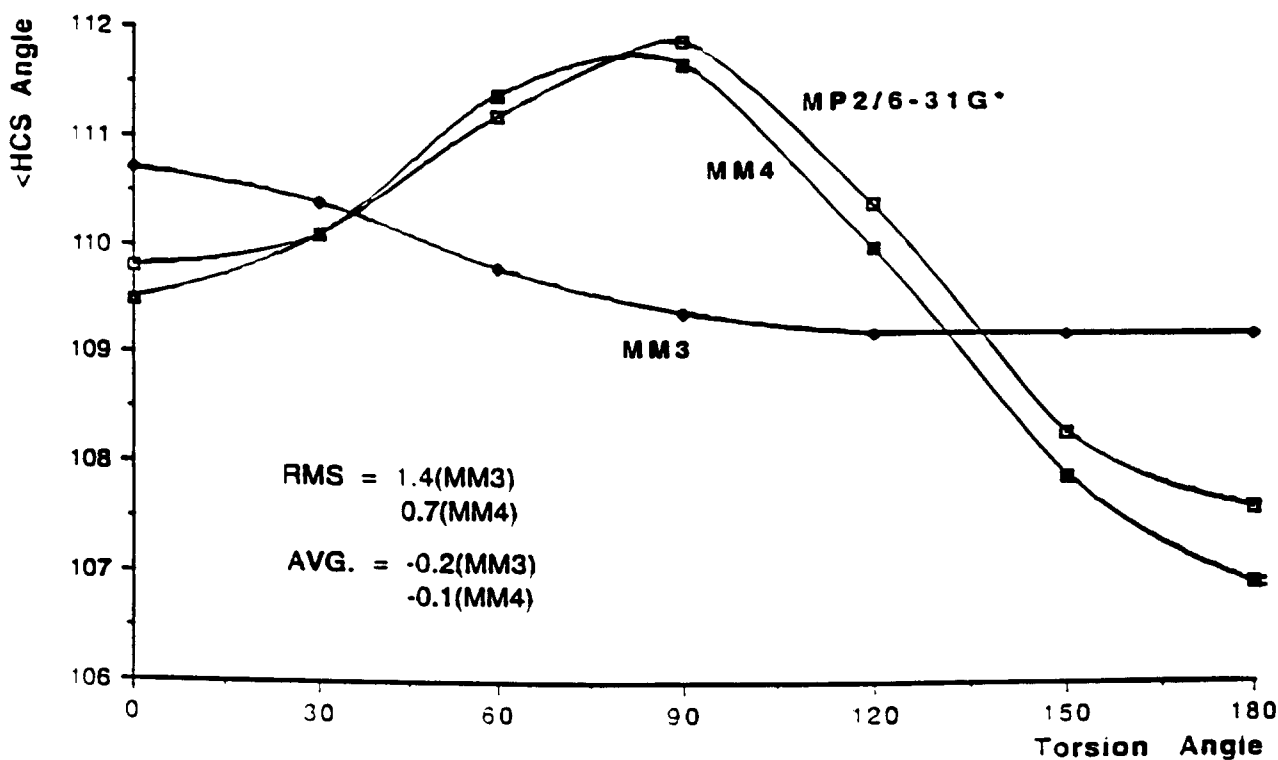


FIGURE 3. The variation of the HCS angle in dimethylsulfide as a function of the CSCH torsional angle.

moments of inertia increase by about 1%. However, in some cases, the difference between the r_z and r_g structures is rather different from normal.

After this work had been completed we had occasion to examine the standard literature method for the conversion of r_g into r_z .⁶⁷ This conversion involves the vibrational amplitudes of the atoms in question, and various approximations are made in the course of the calculation. Our studies showed that some of these approximations were rather crude in cases where the vibrational amplitudes were somewhat larger than usual. Such cases involve vibrations of hydrogen atoms, and of first row atoms that are in shallow, and hence broad, potential wells, particularly the torsional wells in open chain compounds. For these cases, and possibly others, it was found that better approximations were needed to convert r_g into r_z , and this problem is fully discussed elsewhere.⁶⁸ However, by the time that this problem was uncovered, we had already used the literature conversion to calculate moments of inertia of hydrocarbons (and that information is carried over into this work). It was accordingly decided not to go back to the beginning of the hydrocarbon work and reparameterize the geometric quantities to better fit these moments of inertia, although this could be done. The

changes in the r_z values as calculated by the better method (less approximations) do not on the whole differ much from those calculated by the earlier method. In a few cases the errors given by the literature method are about 1% of the number being calculated, but for the most part they are of the order of 0.1%. Accordingly, we have continued to use the earlier described parameterization,⁶ but in the tables herein we have shown the r_z values that are recalculated according to the more accurate interconversion.

Dipole moments have also been determined for a number of the compounds under investigation in this study, mostly from Stark effect measurements in microwave spectroscopy. Comparison of the experimental and calculated dipole moments is shown as Table XIV.

Vibrational Spectra

MM4 also contains a spectroscopic term not present in MM3 that was designed to improve the calculation of the spectra of saturated hydrocarbons, which is a bend-torsion-bend term. This is a mechanical (Class 2) term, and it permits us to calculate the spectra of alkane molecules a little

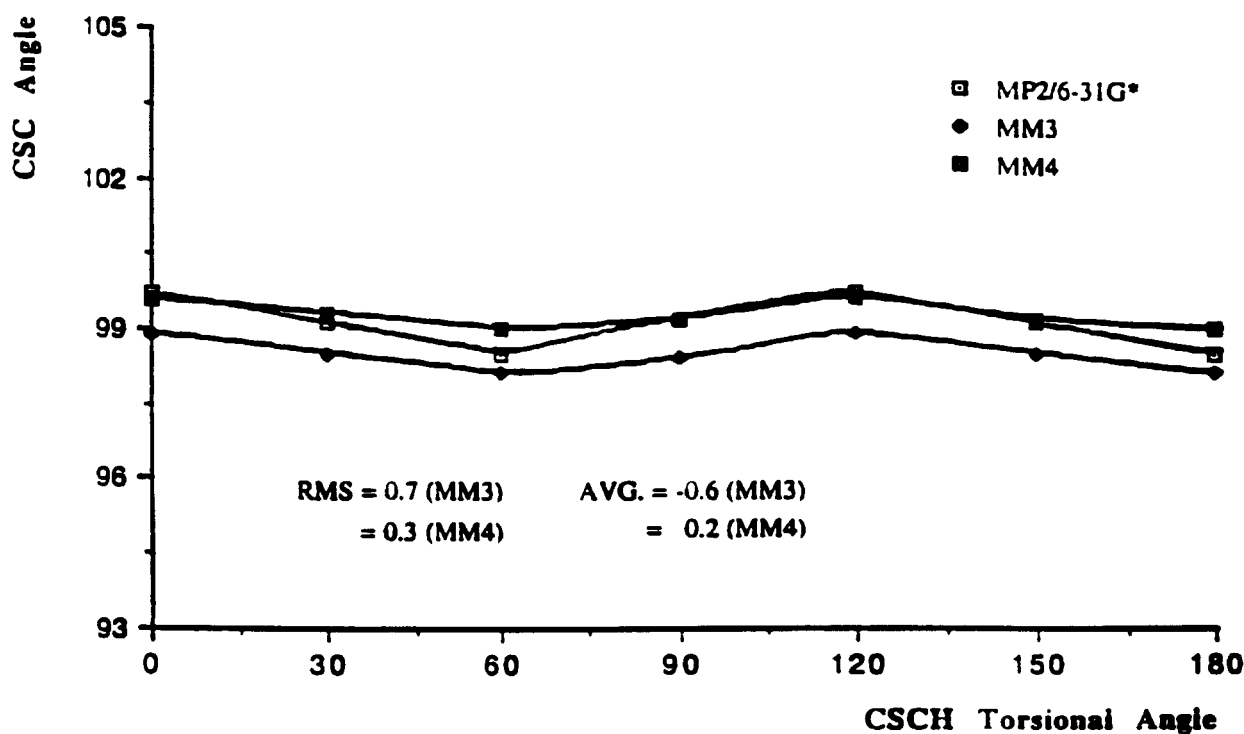


FIGURE 4. The variation of the CSC angle in dimethylsulfide as a function of the CSCH torsional angle.

TABLE I.
MM4 Force Field Parameters for Sulfides and Mercaptans.^a

1. Torsional parameters (kcal/mol) ^b										
Type	V ₁	V ₂	V ₃	K _{BTB}	K _{TB1}	K _{TB2}	K _{TB3}	K _{TB1'}	K _{TB2'}	K _{TB3'}
5-1-15-44	0.000	0.000	0.315	-0.135	-0.012	-0.016	0.000	-0.003	0.000	0.000
5-1-15-1	0.000	0.000	0.540	-0.080	-0.006	-0.020	0.000	0.000	0.000	0.000
1-1-15-44	-0.250	0.000	0.580	-0.100	-0.021	-0.025	0.000	0.004	0.000	0.000
1-1-15-1	0.410	0.000	0.600	0.004	-0.030	-0.023	0.000	0.000	0.000	0.000
15-1-1-15	0.461	-0.144	1.511	-0.130	0.000	-0.003	0.000	0.000	0.000	0.000
5-1-1-15	0.000	0.000	0.460	-0.050	0.000	0.000	0.000	0.000	0.000	0.000
1-1-1-15	-0.420	0.100	0.200	-0.090	0.000	0.000	0.000	0.000	0.000	0.000
44-15-123-5	0.000	0.000	0.320	-0.135	0.000	0.000	0.000	-0.014	-0.016	0.000
5-123-123-15	0.000	0.000	0.200	-0.020	0.000	0.000	0.000	0.000	0.000	0.000
123-15-123-1	0.100	0.000	0.200	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5-1-123-15	0.000	0.330	0.200	-0.050	0.000	0.000	0.000	0.000	0.000	0.000
15-123-123-123	-0.520	0.080	0.250	-0.100	0.000	0.000	0.000	0.000	0.000	0.000
44-15-123-123	-0.370	0.200	0.200	0.000	0.000	0.000	0.000	0.000	0.000	0.000
123-15-123-5	0.000	0.000	0.450	-0.020	0.000	0.000	0.000	0.000	0.000	0.000
15-123-123-123	-0.040	-0.200	0.300	-0.100	0.000	0.000	0.000	0.000	0.000	0.000 *5
123-15-123-123	-0.440	-0.300	0.500	0.000	0.000	0.000	0.000	0.000	0.000	0.000 *5
2. Torsion-stretch parameters (kcal/mol Å) ^c										
Type 1	K _{TS1}	K _{TS2}	K _{TS3}							
X-1-15-Y	0.000	0.000	1.559							
Type 2	K _{TS1}	K _{TS2}	K _{TS3}	K _{TS1'}	K _{TS2'}	K _{TS3'}				
5-1-15-44	0.000	0.000	0.000	0.000	0.000	0.000				
5-1-15-1	0.000	0.900	0.000	0.000	0.000	0.000				
1-1-15-1	0.000	1.439	0.000	0.000	0.000	0.000				
1-1-1-15	-4.798	-4.798	0.000	0.000	0.000	0.000				
15-1-1-15	1.919	1.919	0.000	1.919	1.919	0.000				
3. Bond stretching parameters										
Bond	K _s (mdyn/Å)	I _o (Å)	Bond-mom.							
15-44	3.88	1.332	-1.145							
1-15	2.92	1.814	1.200							
15-123	2.92	1.814	-1.200							
15-123	3.20	1.821	-1.200 *5							
4. Electronegativity effect parameters (Å)										
Bond	Type	Atom type	Attached atom type	Correction						
1	15	15	44	0.0080						
1	1	1	15	-0.0010						
5	1	1	15	-0.0015						
123	15	15	44	0.0080						
5	123	123	15	-0.0022						
123	123	123	15	-0.0015						

TABLE I.
(Continued)

5. VDW parameters

Type	ε (kcal/mol)	R (Å)	
15	0.196	2.090	
15...44	0.600	3.060	H bonding

6. Angle bending parameters

Angle	K_θ (mdyn Å/ rad ²)	θ_0 (deg.)	Type	
5-1-15	0.782	108.9	1	
5-1-15	0.782	108.8	2	
5-1-15	0.782	105.8	3	
1-15-1	0.920	97.2		
1-15-44	0.790	95.2		
1-1-15	0.975	102.6	1	
1-1-15	0.975	105.7	2	
1-1-15	0.975	107.7	3	
5-123-15	0.680	109.1	1	
5-123-15	0.680	107.5	2	
1-123-15	0.975	110.8	2	
15-123-123	0.975	106.2		
44-5-123	0.750	95.6		
123-15-123	0.920	96.5		*5
15-123-123	1.050	108.0	1	*5
15-123-123	1.050	108.0	2	*5
15-123-123	1.050	108.5	3	*5

7. Stretch-bend parameters

Type	K_{sb} (mdyn/rad)	
1-15-1	-0.150	
1-15-44	0.010	
123-15-123	0.280	*5
15-123-123	0.180	*5
5-123-15	0.100	

^a Atom type numbers are 15 for sulfur, 44 for hydrogen attached to sulfur, and 123 for carbon in a five-membered ring. For further information, see ref. 5.

^b K_{TB1} , K_{TB2} , and K_{TB3} are onefold, twofold, and threefold torsion-bend parameters involving the first three atoms in the specific dihedral angle, while $K_{TB1'}$, $K_{TB2'}$, and $K_{TB3'}$ refer to the angle involving last three atoms.

^c Type 1 is the bond change for the central bond and Type 2 is the bond change for the terminal bonds. Type 2 torsion-stretch parameters for A-B-C-D dihedral angle, K_{TS1} , K_{TS2} , and K_{TS3} are onefold, twofold, and threefold parameters for A-B bond, while $K_{TS1'}$, $K_{TS2'}$, and $K_{TS3'}$ refer to the C-D bond.

better than was possible with MM3. Similar small improvements should result in the spectra of other functionalized molecules when MM3 and MM4 are compared, to the extent that such molecules may be considered as perturbed alkanes. Here again, *ab initio* calculations were used to give

vibrational frequencies that were not available from experiment. We used a total of 64 experimental and 96 *ab initio* frequencies, from 7 mercaptans and sulfides (methanethiol, ethanethiol, dimethylsulfide, *trans*- and *gauche*-methylethylsulfide, ethane-1,2-dithiol, and thiocyclopentane). The results,

TABLE II.
Comparison of Calculated and Experimental Geometries of Methanethiol.

Bond length (Å) and bond angles (°)				
Parameter	MM3	MM4	MW (r_z) ²¹	MW (r_z) ²²
C—S	1.825	1.816	1.819 (5)	1.8177 (2)
S—H	1.343	1.333	1.336 (10)	1.3291 (40)
C—H (avg.)	1.112	1.110	1.091 (10)	1.1039 (20)
Φ ^a	0.2	2.9	2.2 (5)	/
CSH	96.8	97.2	96.5 (5)	100.27 (17)
HCH (avg.)	109.4	108.8	109.75 (5)	110.27 (17)
Moments of inertia				
	r_g	r_z	MW (r_z) ²²	
I_a	0.838/—	0.802/—	0.493 ^b	
I_b	6.559/0.87%	6.508/0.09%	6.502	
I_c	6.845/1.00%	6.780/0.04%	6.777	

^a The tilt angle of the methyl group.
^b The rotational constant *A* may be considerably in error because of its sensitivity to the barrier height and certain approximations. The calculated error is therefore not meaningful. The moments of inertia from ref. 22 are used here for comparison.

as anticipated, are somewhat better with MM4. The rms error from the experimental^{14–20}/*ab initio* frequencies is 25 cm^{–1} for MM4, as compared to 41 cm^{–1} for MM3. This improvement, as with the alkanes, is not a result of many small improvements, but rather a result of a few very significant improvements that result from a single type of term.

It is perhaps worth pointing out that the important additional types of terms required to improve the MM4 structures and spectra relative to those for MM3 for hydrocarbons and sulfides are just two in number, a torsion–bend interaction, and a bend–torsion–bend interaction. The first of these has a substantial effect upon the geometries of the molecules, but a negligible effect on spectra. The second has a substantial effect on spectra, but a negligible effect on geometries. Although they may be formally similar from the physicist’s point of view (they are both torsion–bend interactions in the force constant matrix), they result from unrelated phenomena, and from the chemist’s point of view they are quite different. We regard the geometric effect as quite important, because if one cannot get the geometries correct, then most other quantities cannot be correctly calculated. On the other hand, the effect of the improved spectra is mainly esthetic. The bend–torsion–bend term has an effect that can best be seen in the following way. If we consider ethane as composed of two rigid methyl groups, and then we bend them rela-

tive to one another in either a symmetric, or in an antisymmetric mode, these correspond to two different bending frequencies, but they depend upon the same bending constant (C—C—H). In MM3 there is no bend–bend or bend–torsion–bend interaction term, and the splitting of these two frequencies is wrong. They can both be moved up or down by adjusting the bending constant, but the splitting between them cannot be changed. Thus in MM3 there are errors of +86 and –126 cm^{–1} in these frequencies. The extra interaction element allows us to bring these two frequencies much closer together (with corresponding errors of –16 and +10 cm^{–1} in MM4). Of course, it is satisfying to get the frequencies accurately, but as far as we can determine, the consequences of the better frequencies for MM4 relative to MM3 are negligible in all respects. It might be thought that they would make a difference in cumulative properties like entropy, but they do not. The reason is that (apart from the fact that the frequencies are pretty high and thus contribute significantly to the entropy only at elevated temperatures), while a systematic error in frequencies would lead to additive quantities like the entropies being systematically wrong, in this case (a splitting error) the error introduced from a high frequency is approximately canceled by that from the corresponding low frequency, and the overall effect is quite small. One can also imagine distortions of molecules that result from these frequencies being too high or too low, and in

TABLE III.
Comparison of Calculated and Experimental Geometries of Ethanethiol.

Bond length (Å) and bond angles (°)			
Parameter	<i>Gauche</i> (C ₁)		
	MM3	MM4	MW (<i>r_s</i>) ²³
C—C	1.529	1.533	1.528 (7)
C—S	1.833	1.823	1.814 (9)
S—H	1.343	1.333	1.336 (10)
CCS	111.7	113.29	113.69 (48)
CSH	97.0	96.54	96.00 (57)
SCH (<i>gauche</i>)	110.1	111.18	/
SCH (<i>trans</i>)	109.8	107.67	/
CCSH	60.0	63.9	61.75 (97)
Moments of inertia			
	<i>r_g</i>	<i>r_z</i>	MW (<i>r_s</i>) ²³
<i>I_a</i>	18.36/4.44%	17.6288/0.28%	17.5801
<i>I_b</i>	95.17/– 0.29%	95.8873/0.46%	95.4480
<i>I_c</i>	104.53/0.24%	104.6952/0.39%	104.2834
<i>Trans</i> (C _s)			
Parameter	MM3	MM4	MW (<i>r_s</i>) ²³
C—C	1.533	1.534	1.529 (6)
C—S	1.833	1.826	1.820 (5)
S—H	1.343	1.333	1.322 (6)
CCS	111.10	108.56	108.57 (32)
CSH	96.70	96.81	96.22 (38)
SCH	110.2	111.49	/
CCSH	180.00	180.00	180.00
Moments of inertia			
	<i>r_g</i>	<i>r_z</i>	MW (<i>r_s</i>) ²³
<i>I_a</i>	17.51/– 1.52%	17.7998/0.09%	17.784
<i>I_b</i>	95.63/3.81%	92.5412/0.45%	92.124
<i>I_c</i>	106.67/3.04%	104.0861/0.55%	103.520

principle these could be detectable experimentally in properly chosen structures with built-in distortions. However, we have not been able to detect any such discrepancies, and conclude that they must be very small. Finally, for larger, more interesting molecules, these vibrations are buried in the “fingerprint region” of the infrared, and are unidentifiable.

The MM3 and MM4 calculated vibrational spectra are presented in Tables XV–XXI together with the corresponding experimental and *ab initio* results. For methylethylsulfide and thiacyclopentane, since there were no experimental spectro-

scopic data available, *ab initio* calculations were carried out (the spectra of these two molecules are available as Supplementary Material). The *ab initio* frequencies are generally scaled down to 95% of original values for comparison, because the frequencies obtained from the MP2 method are generally 3–5% too high on the average. However, the C–H stretching frequencies in this work are scaled down more. The scale factor applied here (0.930, except for thiacyclopentane where 0.920 is used) is based on the comparison between the experimental data and the MP2 results for the available frequencies.

TABLE IV.
Comparison of Calculated and Experimental Geometries of Dimethylsulfide.

Bond length (Å) and bond angles (°)				
Parameter	MM3	MM4	ED (r_g) ²⁴	MW (r_s) ²⁵
C—S	1.808	1.811	1.807 (2)	1.802 (1)
C—H	1.112	1.110	1.116 (3)	1.090
CSC	98.1	98.96	99.05 (4)	98.80 (15)
SCH (gauche)	109.8	111.28	/	110.77 (30)
SCH (trans)	109.2	107.21	/	106.68 (60)
Φ ^b	0.4	2.7	2.4	/
Moments of inertia				
	r_g	r_z		MW ²⁶
I_a	29.10/2.03%	28.4948/0.42%	/	28.376
I_b	65.93/— 0.58%	66.8707/0.84%	/	66.314
I_c	88.37/— 0.02%	88.9082/0.59%	/	88.387

^a The structural parameters correspond to the staggered conformer.

^b The tilt angle of the methyl group.

TABLE V.
Comparison of Calculated and Experimental Geometries of Methylethylsulfide.^a

Bond length (Å) and bond angles (°)						
Parameter	<i>Gauche</i> (C ₁)					
	MM3 (<i>r_g</i>)	MM4 (<i>r_g</i>)	ED (<i>r_g</i>) ²⁷	MM4 (<i>r_e</i>)	MP2/6-31G*	
C—C	1.534	1.534	1.536 (8)	1.526	1.524	
C—H (avg.)	1.113	1.111	1.111 (8)	1.093	1.093	
C—S (Methyl)	1.810	1.813	1.806 (27)	1.805	1.808	
C—S (Methylene)	1.820	1.820	1.818 (27)	1.812	1.815	
C—S (avg.)	1.815	1.816	1.813 (4)	1.808	1.812	
CSC	99.6	100.1	97.1 (1.1)	/	99.9	
CCS	112.5	114.5	114.0 (0.5)	/	114.6	
CCSC	72.3	69.7	66 (9)	/	68.8	
Moments of inertia						
	<i>r_g</i> (MM3)	<i>r_z</i> (MM4)	Mw ²⁸			
<i>I_a</i>	52.9919/1.38%	52.4174/0.28%	52.2710			
<i>I_b</i>	129.4440/0.40%	130.3573/1.11%	128.9236			
<i>I_c</i>	157.2289/— 0.47%	159.3462/0.88%	157.9638			
Trans (C _s)						
Parameter	MM3 (<i>r_g</i>)	MM4 (<i>r_g</i>)	ED (<i>r_g</i>) ²⁷	MM4 (<i>r_e</i>)	MP2/6-31G*	MW ²⁹
C—C	1.533	1.534	1.536 (8)	1.527	1.524	1.530 (4)
C—H (avg.)	1.113	1.111	1.111 (8)	1.093	1.094	1.090
C—S (methyl)	1.808	1.811	1.806 (27)	1.803	1.807	1.804 (4)
C—S (methylene)	1.816	1.820	1.818 (27)	1.812	1.814	1.804 (4)
C—S (avg.)	1.812	1.815	1.813 (4)	1.808	1.811	/
CSC	98.1	98.9	97.1 (1.1)	/	98.9	99.0 (2)
CCS	111.0	108.7	114.0 (0.5)	/	110.0	109.5 (3)
CCSC	180.0	180.0	180.0	/	179.9	/

TABLE V.
(Continued)

Bond length (Å) and bond angles (°)

	Moments of inertia		
	r_g (MM3)	r_z (MM4)	MW ^b
I_a	5.375/2.34%	5.2481/− 0.07%	5.252
I_b	26.558/0.38%	26.3944/− 0.24%	26.458
I_c	30.304/0.68%	30.0970/− 0.00%	30.099

^a The geometrical parameters of the two conformers in this ED study were assumed to be equal except for the dihedral angle about the C(methylene)—S bond.

^b Moments of inertia obtained from the best-fit rotational constants corresponding to the r_g structure of the *trans* conformer derived from the combined analysis of ED and MW data (ref. 29).

TABLE IX.
Comparison of Calculated and Experimental Geometries of Di-*t*-Butylsulfide (C₂).^c

Bond length (Å) and bond angles (°)

Parameter	MM3	MM	ED (r_g) ³³
C—C (avg.)	1.540	1.536	1.539 (3)
C—S	1.852	1.849	1.854 (5)
C—H (avg.)	1.112	1.111	1.127 (4)
S2C1C4	106.2	102.9	102.2 (9)
CSC	113.9	112.7	113.2 (12)
CCC (avg.)	109.2	109.7	109.6 (5)
CCH (avg.)	111.9	111.9	111.2 (11)
C3S2C1C4	165.1	166.3	168 (8)
H10C4C1S2	179.2	179.3	180 ^b
H25C9C1S2	173.4	171.1	171 (9)
H19C7C1S2	174.3	172.2	171 (9)
Tilt ^a	3.7	6.3	7.1 (20)

^a The tilt angle of the *t*-butyl group is the angle between the C—S bond and the line from the carbon to the point in the plane containing the three attached methyls which is equidistant from all of them.

^b These are assumed values.

^c The number system is shown in Figure 9.

The largest errors in the calculated spectra relative to experiment occur in ethane-1,2-dithiol. There is a HCS bending and two CH₂ wagging modes in ethanethiol for which the MM4 calculated values do not agree with the experiment.²⁰ The experimental frequency at 1292 cm^{−1} was assigned earlier to both CH₂ wagging (A_g) and CH₂ twisting (B_g) in the IR spectrum.²⁰ We agree with the latter assignment (the MM4 and *ab initio* values are 1288 and 1280 cm^{−1} for this vibration) but not with the former (MM4 value 1436 cm^{−1}). We believe that this vibration is truly unobserved, but does not lie under the 1292 cm^{−1} frequency. (The *ab initio* value is 1335 cm^{−1}.) The CSH bend-

TABLE XI.
Comparison of Calculated and Experimental Geometries of 7-Thiabicyclo[2.2.1]heptane (C_{2v}).^c

Bond length (Å) and bond angles (°)

Parameter	MM3	MM4	ED (r_g) ³⁷
C1—C2	1.545	1.545	1.538(6)
C2—C3	1.559	1.565	1.561(15)
C—S	1.836	1.831	1.837(4)
CSC	81.1	81.4	80.2(8)

Moments of inertia			
	r_g (MM3)	r_z (MM4)	MW/ED ^a
I_a	30.8020/0.91%	30.6214/0.31%	30.5253
I_b	31.8787/0.41%	31.8014/0.17%	31.7485
I_c	34.5151/0.35%	34.2914/− 0.30%	34.3937

^a The moments of inertia were obtained from the combined analysis of ED and MW data from ref. 38.

ing was assigned at 800 cm^{−1} from the IR spectrum,²⁰ while the MP2/6-31G* calculation gives 891 cm^{−1} after the scaling. Furthermore, the analogous mode in ethanethiol was found at 870 cm^{−1}. The *ab initio* values were therefore used for the “experimental” values. with these reassignments our rms error is 39 cm^{−1}, still large, but much reduced from the MM3 value of 67 cm^{−1}. One reason for this rather large rms error may be that the observed spectrum is from liquid phase measurements.

It was of interest to carry out more studies on the conformational stability of ethanedithiol because of the hydrogen bonding that could be present in some conformers. Experimental data³⁴ have shown that the conformers with an anti S—C—C—S geometry were more stable than the gauche forms (Table XIII). Applying the *ab initio* method at the MP2/6-31G** level, eight stable conform-

TABLE XIII.
Comparison of Calculated and Experimental Geometries of Ethane-1,2-dithiol.

Bond length (Å) and bond angles (°)					
Parameter	MM3		MM4		ED(r_g) ³⁴
	agg'	avg. ^a	agg'	avg. ^a	
C—C	1.539	1.539	1.539	1.538	1.537 (6)
C—H	1.114	1.114	1.112	1.112	1.118 (11)
C—S	1.835	1.835	1.827	1.831	1.824 (2)
S—H	1.343	1.343	1.333	1.333	1.373 (15)
CCS	11.21	112.2	112.3	113.6	113.1 (4)
HCH	106.3	106.2	105.9 _{ave}	105.8	103.7 (57)
CCH (avg.)	109.3	109.3	109.1	109.1	111.1 (13)
SCH (avg.)	109.9	109.8	110.2	109.4	108.8 (13)
SCCS	70.8	/	68.7	/	69.0 (15)
C1C2S4H10	180.0	/	179.7	/	− 141 (22)
C2C1S3H9	− 60.4	/	− 65.1	/	− 40 (30)
S...H	2.797	/	2.882	/	~ 2.70 (8)
S...S	3.492	/	3.489	/	~ 3.50
Moments of inertia					
	r_g (MM3) agg'		r_z (MM4) ^b agg'		MW ³⁵
I_a	9.169/1.53%		9.0233/ − 0.09%		9.031
I_b	37.517/0.10%		37.4304/ − 0.13%		37.478
I_c	43.621/0.61%		43.4402/0.19%		43.358

^a Boltzmann-weighted averages.
^b The structure fits the experimental moments of inertia and dipole moment.

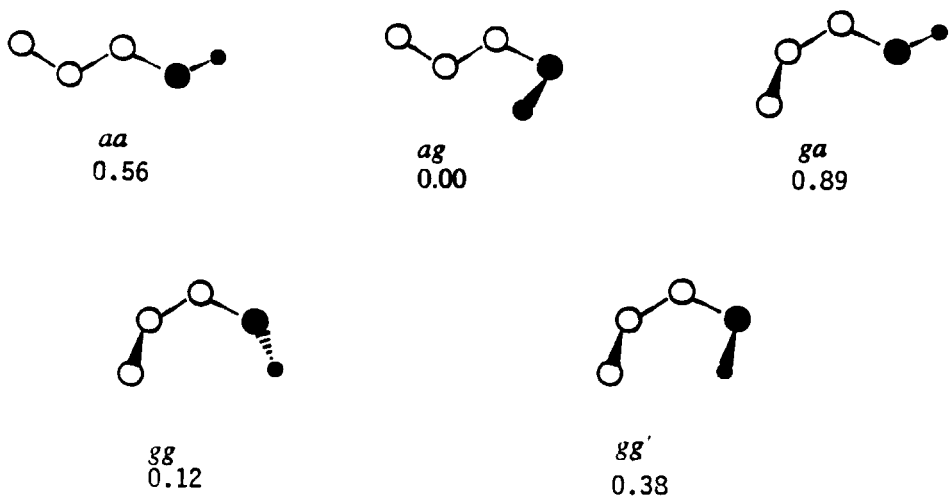


FIGURE 7. The MM4 Energies of 1-propanethiol (ΔE). The first letter refers to the conformation around the C—C bond and the second to the conformation around the C—S bond. (○) Carbon; (●) sulfur; (●) hydrogen.

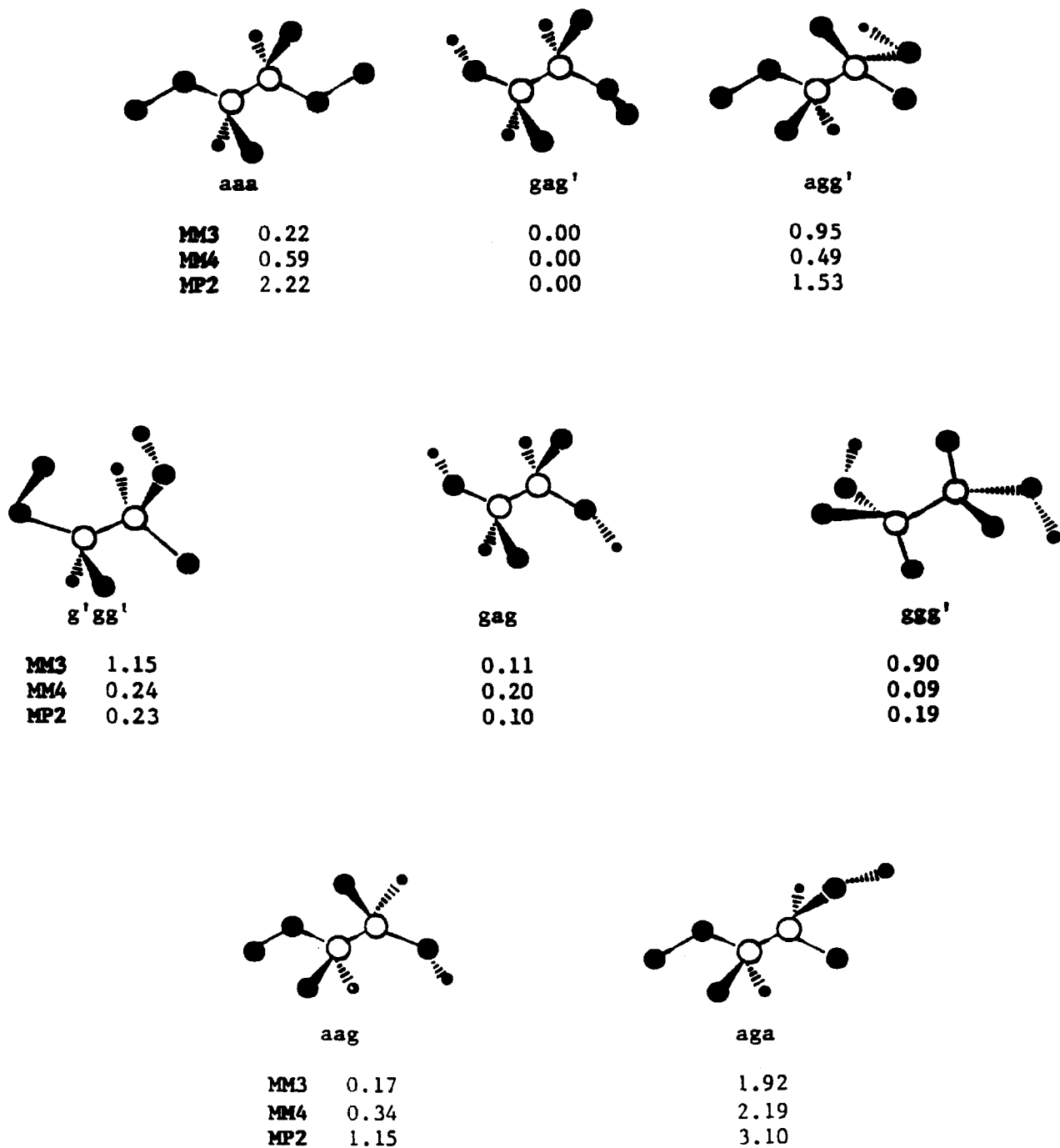


FIGURE 10. The conformers of ethane-1,2-dithiol. (○) Carbon; (●) sulfur; (●) hydrogen.

		NMR ⁶⁶	MM3	MM4
		1.42(7)	1.03	1.18
		1.40(7)	1.60	1.26
		1.80(10)	1.82	1.78
		0.60(5)	0.27	0.49
		0.38(2)	0.76	0.57
		0.02(1)	-0.56	-0.09
		0.16(2)	-0.53	-0.06

FIGURE 11. The conformational equilibria of mono- and dimethylthianes.

ers, which are listed in Table XIII and shown in Figure 10, were found. The gag' and ggg' conformers are the two most stable conformers for the anti and gauche S—C—C—S torsions, respectively. In MM4 parameterization of the S—C—C—S torsion, we weighted those conformations nine times heavier than the other six in an effort to fit better to the low energy conformations. With the final MM4 force field, the rms error for the relative energies of the eight conformers is 0.81 kcal/mol, compared with 1.02 kcal/mol for MM3. While this fit is still

poor, the MP2/6-31G** numbers are probably not very accurate (see ref. 66 for an analogous case), so we have decided to leave the problem at this point for now.

Conformational Equilibria

The rotational energy barriers and conformational energy differences were also calculated, and the results are presented in Tables XXII–XXIV.

TABLE XV.
Vibrational Spectrum of Methanethiol (C_s) (cm^{-1}).

IR (gas) ¹⁴	Sym.	MM3	MM4	Diff. (MM4-IR)	Assignment
3000 ^a	A'	2986	2997	-3	Asym. C—H str.
2807 ^a	A'	2879	2895	25	Sym. C—H str.
2605	A'	2585	2591	-14	S—H str.
1453	A'	1414	1417	-36	Asym. CH ₃ def.
1332	A'	1351	1298	-34	Sym. CH ₃ def.
1072	A'	1013	1051	-21	CH ₃ rock.
802	A'	823	794	-8	CSH bend.
710	A'	695	702	-8	CS str.
3000 ^a	A''	2984	2998	-2	Asym. C—H str.
1444	A''	1420	1393	-51	Asym. CH ₃ def.
956	A''	1008	951	-5	CH ₃ rock.
/	A''	249	247	/	Torsion
RMS		31	24		
Avg.		-8	-13		

^a Because the observed C—H stretching frequencies in ref. 14 seemed to be higher than usual for this class of compounds, the C—H stretching frequencies reported in earlier literature¹⁵ were used instead.

TABLE XVI.
Vibrational Spectrum of *gauche*-Ethanethiol (C_1) (cm^{-1}).

IR (gas) ¹⁶	MM3	MM4	Diff. (MM4-IR)	Assignment
2971 ^a	2968	2974	3	Asym. CH ₃ str.
2946 ^a	2966	2971	25	Asym. CH ₃ str.
2940 ^a	2932	2943	3	Asym. CH ₂ str.
2886 ^a	2885	2897	11	Sym. CH ₃ str.
/	2870	2879	/	Sym. CH ₂ str.
2590 ^a	2585	2591	1	S—H str.
1457	1492	1512	55	CH ₂ scis.
1457	1467	1456	-0	Asym. CH ₃ def.
1382	1457	1448	66	Asym. CH ₃ def.
/	1442	1433	/	Sym. CH ₃ def.
1309	1376	1365	56	CH ₂ wagging
1277	1269	1307	30	CH ₂ twist
1101	1034	1105	8	CH ₃ rock
1049	1015	1046	-3	CH ₃ rock
969	974	983	14	C—C str.
870	849	867	-3	CSH bending
735	800	744	9	CH ₂ rock
663	662	663	0	C—S str.
317	333	327	10	CCS bending
246 ^a	267	265	19	CH ₃ torsion
191 ^a	204	228	37	CSSH torsion
RMS	33	27		
Avg.	9	17		

^a The values are from gas phase Raman spectra reported in ref. 17.

TABLE XVII.
Vibrational Spectrum of Dimethylsulfide (C_{2v}) (cm⁻¹).

IR (gas) ¹⁸	Sym.	MM3	MM4	Diff. (MM4-IR)	Assignment
2990	A1	2987	2998	8	Asym. CH ₃ str.
2990	B2	2986	2998	8	Asym. CH ₃ str.
/	A2	2986	2998	/	Asym. CH ₃ str.
2990	B1	2986	2996	6	Asym. CH ₃ str.
2915	A1	2880	2895	-20	Sym. CH ₃ str.
2850	B1	2879	2895	45	Sym. CH ₃ str.
1456	A1	1417	1413	-43	Asym. CH ₃ def.
1440	B1	1415	1413	-27	Asym. CH ₃ def.
1420	B2	1435	1399	-21	Asym. CH ₃ def.
/	A2	1426	1395	/	Asym. CH ₃ def.
1317	A1	1355	1299	-18	Sym. CH ₃ def.
1317	B1	1352	1291	-26	Sym. CH ₃ def.
1036	A1	1026	1003	-33	CH ₃ rock
1005	B2	1021	981	-24	CH ₃ rock
972	B1	1010	967	-5	CH ₃ rock
/	A2	1001	951	/	CH ₃ rock
703	B1	701	704	1	C—S asym. str.
684	A1	683	700	16	C—S sym. str.
(285) ^a	A1	284	271	-14	CSC bending
/	B2	219	204	/	CH ₃ torsion
/	A2	187	179	/	CSCH torsion
RMS		24	23		
Avg.		3	-9		

^a The value is from IR spectra reported in ref. 19.

TABLE XVIII.
Vibrational Spectrum of *gauche*-Methylethylsulfide (C₁) (cm⁻¹).

MP2/6-31G* ^a	MM3	MM4	Diff. (MM4- <i>ab initio</i>)	Assignment
2994	2994	3003	9	Asym. CH ₃ str.
2987	2986	2997	10	Asym. CH ₃ str.
2982	2976	2980	-2	Asym. CH ₃ (CH ₂) str.
2970	2966	2971	1	Asym. CH ₃ (CH ₂) str.
2949	2932	2942	-7	Asym. CH ₂ str.
2896	2887	2897	1	Sym. CH ₃ (CH ₂), CH ₂ str.
2893	2883	2897	4	Sym. CH ₃ str.
2889	2873	2881	-8	Sym. CH ₃ (CH ₂), CH ₂ str.
1486	1476	1525	39	Asym. CH ₃ (CH ₂) def.
1480	1459	1463	-17	Asym. CH ₃ (CH ₂) def.
1470	1437	1416	-54	Asym. CH ₃ def.
1455	1503	1448	-7	CH ₂ def.
1449	1446	1440	-9	CH ₂ def.
1395	1414	1402	7	Asym. CH ₃ def.
1367	1384	1371	4	Sym. CH ₃ (CH ₂) def.
1299	1356	1298	-1	Sym. CH ₃ def.
1262	1278	1319	57	CH ₂ twist
1077	1032	1077	0	CH ₃ (CH ₂)CH ₃ ,CH ₂ rock
1054	1023	1045	-9	CH ₃ (CH ₂) rock, C—C str.
980	1010	994	14	CH ₃ ,CH ₃ (CH ₂) rock

TABLE XVIII.
(Continued)

MP2/6-31G* ^a	MM3	MM4	Diff. (MM4- <i>ab initio</i>)	Assignment
974	971	973	-1	C—C str.
959	1008	960	1	CH ₃ , CH ₃ (CH ₂) rock
751	841	772	21	CH ₂ rock
734	694	694	-40	C—S str.
662	640	647	-15	C—S str.
345	349	340	-5	CCS bending
277	279	268	-9	CH ₃ torsion
222	249	236	14	CSC bending
169	201	193	24	CH ₃ torsion
82	86	90	8	CSCC torsion
RMS	32	20		
Avg.	13	1		

^a The C—H stretching frequencies are scaled down to 93% of original values, while the others are scaled down to 95%. These scale factors are used elsewhere in this work.

TABLE XXI.
Vibrational Spectrum of Ethane-1,2-dithiol (C₂H₆S₂) (cm⁻¹).

IR (liquid) ²⁰	MP2/6-31G* ^a	MM3	MM4	Sym.	Diff. (MM4-IR)	Assignment
2920	2914	2881	2905	Ag	-15	C—H str.
2570	2647	2586	2592	Ag	22	S—H str.
1420	1479	1521	1498	Ag	78	CH ₂ bending
1292 ^b	1335	1440	1436	Ag	101	CH ₂ wagging
1035	1086	998	1043	Ag	8	C—C str.
800 ^b	891	825	881	Ag	-10	CSH def.
718	738	726	742	Ag	24	C—S str.
299	278	273	292	Ag	-7	CCS def.
2968	2986	2931	2950	Au	-18	C—H str.
1155	1123	1296	1202	Au	47	CH ₂ twist
718	772	807	767	Au	49	CH ₂ rock
/	140	181	202	Au	/	C—S torsion
/	79	113	129	Au	/	C—C torsion
2968	2969	2927	2945	Bg	-23	C—H str.
1292	1280	1278	1288	Bg	-4	CH ₂ twist
1030	977	956	1004	Bg	-26	CH ₂ rock
255	143	195	218	Bg	-37	C—S torsion
2920	2922	2872	2897	Bu	-23	C—H str.
2570	2647	2586	2592	Bu	22	S—H str.
1428	1481	1471	1474	Bu	36	CH ₂ bending
1220 ^b	1240	1371	1305	Bu	65	CH ₂ wagging
890	878	831	889	Bu	-1	CSH def.
600	727	699	698	Bu	-1	C—S str.
/	198	232	234	Bu	/	CCS def.
RMS		67	39			
Avg.		8	14			

^a The wave numbers for C—H stretching are scaled down to 93% of original values, while the others are scaled down to 95%.

^b MP2/6-31G* values used for RMS calculation.

TABLE XXII.
Conformational Energy Differences (kcal / mol)^a.

Compound	Conformation	MM3	MM4	Exp.		Ref.
Ethanethiol	<i>a-g</i>	0.29	0.39	0.41 ± 0.04	Δ <i>H</i>	41
1-Propanethiol ^b	<i>aa-ag</i>	0.28	0.40	0.39 ± 0.11	Δ <i>H</i>	30
	<i>ga-aa</i>	0.69	0.34	0.44 ^c	Δ <i>E</i>	This work
2-Propanethiol ^b	<i>g-a</i>	0.28	0.06	0.06 ± 0.03	Δ <i>G</i>	31
Methylethylsulfide	<i>a-g</i>	−0.13	0.12	0.24 ~ 0.65	Δ <i>G</i>	27
Isopropylmethylsulfide	C ₁ -C _s	−0.45	−0.32	~ 0.00	Δ <i>E</i>	45
Diethylsulfide	<i>ag-gg</i> (liq.)	−0.20	−0.34	−0.04 ± 0.05	Δ <i>H</i>	46
	<i>aa-ag</i> (liq.)	−0.31	−0.25	0.46 ± 0.10	Δ <i>H</i>	46
Diisopropylsulfide ^c	I	0.00	0.00	0.00 ^c	Δ <i>E</i>	This work
	II	0.76	0.97	1.11 ^c	Δ <i>E</i>	This work
	III	1.14	1.29	1.72 ^c	Δ <i>E</i>	This work
	IV	2.42	2.10	2.40 ^c	Δ <i>E</i>	This work
	V	4.63	3.87	4.99 ^c	Δ <i>E</i>	This work
Thiacyclohexane	<i>tw-ch</i>	5.07	4.98	4.02	Δ <i>H</i>	47
Cyclohexanethiol (<i>ch</i>)	<i>ax-eq</i>	1.94 ^d	1.44 ^d	~ 1.10	Δ <i>G</i>	48
	<i>tw-ch</i>	4.89	5.38	~ 5.5	Δ <i>G</i>	48

^a Symbols *a*, *g*, *tw*, and *ch*, refer to *anti*, *gauche*, *twist-boat*, and *chair* conformations, respectively, and *eq* and axial represents an equatorial and axial bond.
^b First letter refers to conformations around C—C bonds, the second to conformations around C—S bonds, and thereafter in turn.
^c These data are from *ab initio* calculations at the MP2/6-31G* level. For definition of the conformers of diisopropylsulfide, refer to Figure 6.
^d Boltzmann-averaged free energy differences.

MM3 usually used relative steric energies in fitting parameters for the rotational barriers and conformational energy differences. The MM4 force field allows us to calculate enthalpy (*H*), free energy (*G*), and energy (*E*), and then the proper comparisons can be made depending on the source of the experimental data (IR intensity variations with temperature, NMR, or *ab initio* calculations, for example, respectively), and the parameterization was carried out by fitting to the particular thermodynamic quantity what was observed in each case. The resulting force field is expected to be, and is, more accurate.

Several conformational energies are known for methyl-substituted thiacyclohexanes,⁶⁰ and it is, of course, desirable that these be well fit. They were determined by NMR measurements in solution, and hence correspond to Δ*G* values at various temperatures. The structures of several of the compounds examined, together with the experimental values for the equilibria, and the MM3 and MM4 calculated values are displayed in Figure 11. If we begin with the chair form of the thiane ring, and consider a methyl group attached to the 2, 3, or 4 position, the experimental values for the equilibria (Δ*G*) are 1.42, 1.40, and 1.80 kcal/mol, respec-

tively, The 4-methyl compound has an energy difference almost identical to that in the parent hydrocarbon, both experimentally and by all calculations. The other two compounds have smaller energies for the axial structure, relative to the equatorial, by several tenths of a kilocalorie. The fit is somewhat better for MM4 than for MM3.

When we consider dimethyl-substituted thianes, there are a number of possibilities. The compounds that have been studied experimentally were examined, and the data were fit well with MM4 in each case.⁶⁰ The fit for MM3 was not as good, although it was fair (Fig. 11).

Heats of Formation

Heats of formation of sulfides are calculated based on statistical thermodynamics, and they have a more exactly defined physical basis than do those obtained by the MM3 method. The MM3 force field used the bond increment method and steric energies,^{1, 61, 62} while MM4 used bond increments and enthalpies,³ so that the molecular vibrations are explicitly accounted for (rather than aver-

TABLE XXIII.
Energy Barriers of Internal Rotation (kcal / mol)^a.

Compound		MM3	MM4	Exp.	Ref.
Methanethiol	—CH ₃	1.28	1.27	1.27 ± 0.01	21
Dimethylsulfide	—CH ₃	2.25	2.04	2.13	26
Ethanethiol	(<i>g</i>)—CH ₃	3.66	3.44	3.77 ± 0.03	17
	(<i>a</i>)—CH ₃	3.97	3.61	3.31 ± 0.09	41
	<i>g</i> → <i>a</i>	1.25	1.69	1.42	49
	<i>g</i> → <i>g</i>	1.30	2.01	1.76	17
	(<i>ag</i>)—CH ₃	2.70	2.83	3.1	50
1-Propanethiol ^b	(<i>ag</i>) → <i>aa</i>	1.23	1.69	1.43	30
	(C _s)—CH ₃	4.00	3.73	3.75	49
2-Propanethiol	C—S	1.12	2.60	1.98	31
	—CH ₃	4.38	3.50	5.1	51
2-Me-2-propanethiol	C—S	1.01	1.89	1.36	51
	(<i>g</i>) S—CH ₃	2.11	2.01	1.71 ± 0.04	28
Methylethylsulfide	(<i>a</i>) S—CH ₃	2.26	2.05	1.98 ± 0.06	43
	(<i>g</i>) C—CH ₃	3.41	3.26	3.33	52
	(<i>a</i>) C—CH ₃	3.70	3.62	3.93	53
	<i>g</i> → <i>a</i>	1.63	1.72	1.81 ^c	This work
	<i>hf</i> → <i>hf</i>	1.78	2.62	2.76 ^c	This work

^a Symbols *a*, *g*, and *hf* refer to *anti*, *gauche*, and *half-chair* conformations, respectively. All the experimental barriers in ΔE , except the barriers for 2-Me-2-propanethiol, which are differences in enthalpies.

^b The first letter refers to conformations around C—C bonds, the second to conformations around C—S bonds.

^c The barriers were obtained from MP2/6-31G* calculations.

aged into the bond increments, as in MM3). The experimental data were obtained from Refs. 63–65 and are summarized in Table XXV. The parameters required for this class of compounds are bond parameters, C—S and S—H, and the structural parameters for secondary, tertiary, and methyl groups attached to a sulfur atom. An additional energy increment for the structural feature S—C—C—S should also be required to fit a vicinal dithiol. It is found that this latter term, which is expected as a result of the physical interaction of the two C—S bonds, is small (−0.62 kcal/mol), as expected. The least squares fitting to the data gave the parameters and results shown in Tables XXVI and XXVII. The weighted standard deviation is 0.36 kcal/mol, which is approximately the experimental error for this class of compounds.

Eight sulfides and mercaptans were chosen as strainless for the strain energy calculations, and they are listed in Table XXVIII. In Table XXIX are given the calculated strain energies for a selection of compounds of this class.

Supplementary Material: Figures 2, 5, 6, 8, and 9 and Tables VI–VIII, X, XII, XIV, XIX, XX, XXIV, XXV, XXVIII, and XXIX are available from the authors or from the *Journal of Computational Chemistry* website.

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TABLE XXVI.
Heat Parameters for Sulfides and Mercaptans.

Best values:			
C—S = −73.7353	S—H = −90.8667	SEC = −1.5002	TER = −3.2281
S—ME = 1.1379	SCCS = −0.6220		

TABLE XXVII.
Heats of Formation of Sulfides and Mercaptans.^a

WT	Calc.	Exp.	Calc.-Exp.	Exp. Error	Compound
10	-5.20	-5.47	0.27	±0.17	Methanethiol
10	-11.06	-11.07	0.00	±0.14	Ethanethiol
10	-9.02	-8.96	-0.06	±0.14	Dimethylsulfide
10	-16.12	-16.23	0.11	±0.17	1-Propanethiol
7	-14.58	-14.24	-0.34	±0.29	2-Thiabutane
9	-20.09	-19.98	-0.11	±0.19	3-Thiapentane
10	-18.65	-18.21	-0.44	±0.17	2-Propanethiol
9	-21.48	-21.63	0.15	±0.19	3-Me-2-Thiabutane
8	-45.19	-45.15	-0.04	±0.24	Di-t-Butylsulfide
7	-8.00	-8.15	0.15	±0.31	Thiacyclopentane
8	-15.85	-15.18	-0.67	±0.24	Thiacyclohexane
8	-23.39	-22.97	-0.42	±0.22	Cyclohexanethiol
7	-24.74	-24.43	-0.31	±0.26	2-Thiahexane
9	-28.93	-28.99	0.06	±0.19	3,3-Di-Me-2-Thiabutane
8	-22.57	-23.26	0.69	±0.22	2-Me-1-Propanethiol
8	-26.62	-26.20	-0.42	±0.22	2-Me-2-Propanethiol
8	-30.29	-30.38	0.09	±0.24	2-Me-2-Butanethiol
7	-27.14	-28.01	0.87	±0.57	2-Me-3-Thiapentane
5	-34.54	-35.37	0.83	±0.60	2,2-Di-Me-3-Thiapentane
6	-33.85	-33.94	0.09	±0.36	2,4-Di-Me-3-Thiapentane
9	-11.30	-11.41	0.11	±0.18	Cyclopentanethiol
9	-15.32	-15.34	-0.02	±0.19	2-Methiacyclopentane
7	-2.32	-2.32	0.00	±0.26	Ethane-1,2-dithiol

^a The standard deviation = 0.38, based on 23 equations. The weighted standard deviation = 0.36, based on 23 equations.

References

1. U. Burkert and N. L. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, DC, 1982.
2. M. J. Hwang, T. P. Stockfisch, and A. Hagler, *J. Am. Chem. Soc.*, **116**, 2515 (1994).
3. N. L. Allinger and J.-H. Lii, *J. Comput. Chem.*, **17**, 642 (1996).
4. N. L. Allinger, Y.-H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8551, 8566, 8576 (1989).
5. The MM4 program will be available in due course to commercial users from Tripos Associates, 1699 S. Hanley Road, St. Louis, MO 63144. It will be available to academic users from either Tripos Associates or from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.
6. (a) N. Nevins and N. L. Allinger, *J. Comput. Chem.*, **17**, 669 (1996); (b) N. Nevins, J.-H. Lii and N. L. Allinger, *J. Comput. Chem.*, **17**, 695 (1996); (c) N. Nevins and N. L. Allinger, *J. Comput. Chem.*, **17**, 730 (1996); (d) N. L. Allinger, K. Chen, J. A. Katzenellenbogen, S. R. Wilson, and G. M. Anstead, *J. Comput. Chem.*, **17**, 747 (1996).
7. Y. Fan, Dissertation submitted to the University of Georgia in partial fulfillment of the requirements for the Ph.D., 1994.
8. N. L. Allinger, M. R. Imam, M. R. Frierson, Y. H. Yuh, and L. Schafer, *Mathematics and Computational Concepts in Chemistry*, N. Trinajstić, Ed., Ellis Horwood, London, 1986, p.8.
9. L. R. Schmitz and N. L. Allinger, *J. Am. Chem. Soc.*, **112**, 8307 (1990).
10. J. R. Kneisler and N. L. Allinger, *J. Comput. Chem.*, **17**, 757 (1996); L. Nørskov-Lauritsen and N. L. Allinger, *J. Comput. Chem.*, **5**, 326 (1984); G. Jeffrey and R. Taylor, *J. Comput. Chem.*, **1**, 99 (1980); P. Aped, unpublished data included in the MM3 program.
11. N. L. Allinger, M. Quinn, M. Rahman, and K. Chen, *J. Phys. Org. Chem.*, **4**, 647 (1991).
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, J. J. P. Stewart, and J. A. Pople, *Gaussian 92/DFT, Revision F.2*, Gaussian Inc., Pittsburgh, PA, 1993.
13. The zero constant for the C—S—C angle is expected, because if we consider C—S—CH₃ specifically, the three hydrogens together constitute a cylindrically symmetrical shell of orbitals about the S—C bond. As torsion of the methyl occurs, S⁺=CH₂H⁻ type resonance affects the hydrogens in turn. Thus properties such as bond length and bond angle involving individual hydrogens (C—H and S—C—H) are expected to undergo changes, but the C—S—C angle is affected only to the extent that the CH₃ group lacks cylindrical symmetry. Thus for a methyl attached to sulfur we expect a zero constant at the sulfur angle. Actually, the sulfur deforms the methyl slightly, so the symmetry is not quite exact. With CH₂CH₃, for example, the

- deformation would be slightly larger, so the effect should be small but maybe not exactly zero. The H—C—S bond angles, on the other hand, are expected to, and do, undergo large torsionally dependent angular changes.
14. I. W. May, and E. L. Pace, *Spectrochim. Acta*, **24A**, 1605 (1968).
 15. H. W. Thompson, and N. P. Skerrett, *Trans. Faraday Soc.*, **36**, 812 (1940).
 16. H. Wolff and J. Szydowski, *Can. J. Chem.*, **63**, 1708 (1985).
 17. J. R. Durig, W.E. Bucy, C. J. Wurrey, and L. A. Carreira, *J. Phys. Chem.*, **79**, 988 (1975).
 18. Y. Shiro, M. Ohsaku, M. Hayashi, and H. Murata, *Bull. Chem. Soc. Jpn.*, **43**, 609 (1970).
 19. H. W. Thompson, *J. Mol. Spectrosc.*, **9**, 38 (1941)
 20. M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Jpn.*, **38**, 1734 (1965).
 21. (a) T. Kojima, *J. Phys. Soc. Jpn.*, **15**, 1284 (1960); (b) T. Kojima, *J. Phys. Soc. Jpn.*, **12**, 680 (1957).
 22. R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955).
 23. (a) J. Nakagawa, K. Kuwada, and M. Hayashi, *Bull. Chem. Soc. Jpn.*, **49**, 3420 (1976); (b) M. Hayashi, H. Imaishi, and K. Kuwada, *Bull. Chem. Soc. Jpn.*, **47**, 2382 (1974).
 24. T. Mijima, S. Tsuchiya, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **50**, 2564 (1977).
 25. M. Hayashi, N. Nakata, and S. Miyazaki, *J. Mol. Spectrosc.*, **135**, 270 (1989).
 26. L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).
 27. K. Oyanagi and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **51**, 2243 (1978).
 28. M. Adachi, J. Nakagawa, and M. Hayashi, *J. Mol. Spectrosc.*, **91**, 381 (1982)
 29. M. Hayashi, M. Adachi, and J. Nakagawa, *J. Mol. Spectrosc.*, **86**, 129 (1981).
 30. J. Nakagawa and M. Hayashi, *J. Mol. Spectrosc.*, **85**, 327 (1981).
 31. J. H. Griffiths and J. E. Boggs, *J. Mol. Spectrosc.*, **56**, 257 (1975).
 32. H. Takeuchi and S. Konaka, *J. Mol. Struct.*, **240**, 141 (1990).
 33. A. Tsubayama, S. Konaka, and M. Kimura, *J. Mol. Struct.*, **127**, 77 (1985).
 34. S. L. Barkowski, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, **108**, 6898 (1986).
 35. R. N. Nandi, C.-F. Su, and M. D. Harmony, *J. Chem. Phys.*, **81**, 1051 (1984).
 36. Z. Nahlovská, B. Nahlovsky, and H. M. Seip, *Acta. Chem. Scand.*, **23**, 3534 (1969).
 37. T. Fukuyama, K. Oyanagi, and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **49**, 638 (1976).
 38. K. Irie, T. Tanaka, E. Hirota, Y. Tamaru, I. Tabushi, and Z. Yoshida, *27th Annual Meeting of the Chemical Society of Japan*, Nagoya, Japan, 1972.
 39. R. W. Kitchin, T. B. Malloy, Jr., and R. L. Cook, *J. Mol. Spectrosc.*, **57**, 179 (1975).
 40. G. Schultz, A. Kucsmann, and I. Hargittai, *Acta. Chem. Scand. (Series A)*, **42**, 332 (1988).
 41. R. E. Schmidt and C. R. Quade, *J. Chem. Phys.*, **62**, 3863 (1975).
 42. M. Hayashi, H. Imaishi, and K. Kuwada, *Bull. Chem. Soc. Jpn.*, **47**, 2382 (1974).
 43. M. Hayashi, M. Adachi, and J. Nakagawa, *J. Mol. Spectrosc.*, **86**, 129 (1981).
 44. A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman, San Francisco, 1963.
 45. J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Jossenlopp, and G. Waddington, *J. Am. Chem. Soc.*, **77**, 6119 (1955).
 46. M. Ohta, Y. Ogawa, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 380 (1977).
 47. J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, H. F. Messerly, and G. Waddington, *J. Am. Chem. Soc.*, **76**, 2661 (1954).
 48. D. W. Scott and G. A. Crowder, *J. Chem. Phys.*, **46**, 1054 (1967).
 49. D. Smith, J. P. Devlin, and D. W. Scott, *J. Mol. Spectrosc.*, **25**, 174 (1968).
 50. R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Jossenlopp, and G. Waddington, *J. Am. Chem. Soc.*, **78**, 3266 (1956).
 51. J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly, and G. Waddington, *J. Am. Chem. Soc.*, **75**, 1818 (1953).
 52. J. R. Durig, D. A. C. Compton, and M.-R. Jalilian, *J. Phys. Chem.*, **83**, 511 (1979).
 53. D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington, and H. M. Huffman, *J. Am. Chem. Soc.*, **73**, 261 (1951).
 54. M. Hayashi, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).
 55. N. Nogami, H. Sugeta, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **48**, 3573 (1975).
 56. M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 111 (1977).
 57. M. Ohsaku, N. Bingo, H. Fujiwara, and H. Murata, *Bull. Chem. Soc. Jpn.*, **51**, 1539 (1978).
 58. J. L. Bredas, M. Dufey, J. G. Fripiat, and J. M. Andre, *Mol. Phys.*, **49**, 1451 (1983).
 59. M. Ohsaka, and A. Imamura, *Mol. Phys.*, **55**, 331 (1985).
 60. R. L. Willer and E. L. Eliel, *J. Am. Chem. Soc.*, **99**, 1925 (1977); E. L. Eliel and R. L. Willer, *J. Am. Chem. Soc.*, **99**, 1936 (1977). The observed values were obtained in solution at -83°C for compounds 1–3 and -95°C for compounds 4–7. MM4 values are calculated at the same temperature, while the MM3 values are steric energy differences.
 61. N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8855 (1989).
 62. J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, **111**, 8576 (1989).
 63. J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.
 64. J. B. Pedley and J. Rylance, *Sussex-N. P. L. Computer Analyzed Thermochemical Data*, University of Sussex, 1977.
 65. J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd Ed., Chapman & Hall, London, 1986.
 66. C. J. Cramer and D. G. Truhlar, *J. Am. Chem. Soc.*, **116**, 3892 (1994).
 67. K. Kuchitsu and S. J. Cyvin, *Molecular Structures and Vibrations*, S. J. Cyvin, Ed., Elsevier, New York, 1972, p. 196.
 68. B. Ma, J. H. Lii, K. Chen, and N. L. Allinger, *J. Am. Chem. Soc.*, **119**, 2570 (1997).